Supporting Information for 'Excited states of butadiene to chemical accuracy: reconciling theory and experiment'

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Frozen orbital extrapolation

Here we describe how we estimate the very expensive EOM-CCSDT/aug-cc-pVTZ increment for the $1^1B_u^+$ state, as presented in Table 2 in the main text. This calculation was impractical using our hardware resources when freezing only the 4 lowest-lying core 1s orbitals. Our strategy was to therefore freeze more orbitals and compare our results with the less expensive EOM-CR-CCSD(T) calculations, which could be completed without freezing additional orbitals. The results are given in Table 1, where we have given the triples increments and the ratio of the full triples increment to the perturbative increment. We notice that the ratio between the two increments is approximately constant. Therefore, to extrapolate the EOM-CCSDT increment to the level of 4 frozen orbitals, we took the ratio (2.49) from the best EOM-CCSDT result available and scaled the CR(T) value of -0.309 eV by this number. This gave a value of -0.124 eV for our estimated EOM-CCSDT increment.

Table 1: CR-CCSD(T) and EOM-CCSDT incremental corrections (in eV) to the EOM-CCSD vertical excitation energy of the $1^1B_u^+$ state in the aug-cc-pVTZ basis set as a function of the number of frozen orbitals.

Frozen	CCSD	+CR(T)	+T	CR(T)/T
13	6.935	-0.009	-0.006	1.42
12	6.802	-0.055	-0.023	2.42
11	6.709	-0.106	-0.043	2.49
10	6.630	-0.175	-0.070	2.49
9	6.588	-0.224	-0.090	2.49
8	6.496	-0.244		
7	6.476	-0.259		
6	6.443	-0.279		
5	6.382	-0.294		
4	6.365	-0.309		

Many-body frozen orbital expansion

Here we describe the strategy we used to obtain results for the very expensive EOM-CC calculations involving quadruple excitations, where a brute-force computation was intractable. As explained in the main text, most of the calculations were run with 8 electrons uncorrelated and occupying the 4 lowest-lying core 1s orbitals. However, in order to make the quadruples calculations feasible, more orbitals needed to be frozen. Table 2 gives results for the two states at the quadruples level, using different numbers of correlated orbitals with a cc-pVDZ basis set.

Table 2: EOM-CC excitation energy quadruples increments in eV for the dark and bright states in butadiene in a cc-pVDZ basis set as a function of the number of frozen orbitals. The converged values correspond to the +Q increments presented in the main paper. The values marked with * were estimated using the many-body expansion described below.

Frozen	$1^1B_u^+$	$2^1A_g^-$
13	-0.001	+0.004
12	-0.002	-0.006
11	-0.005	-0.017
10	-0.010	-0.033
9	-0.015	-0.057*
8	-0.015	-0.074*
7	-0.014*	

From this table, it appears that the $1^1B_u^+$ quadruples correction is actually quite well converged already with 8 frozen orbitals. The result with 7 frozen orbitals was too expensive to obtain directly and was obtained using a many-body expansion (MBE) in the frozen orbitals. More specifically, we can decompose the exact EOM-CCSDTQ energy in terms of the number of correlated orbitals as

$$E = E_0 + \sum_i^N \Delta E_i + \sum_{i<j}^N \Delta E_{ij} + \sum_{i<j<k}^N \Delta E_{ijk} + \cdots \tag{1}$$

This expansion is exact by definition (if computed to all orders) since

$$\Delta E_i \equiv E_i - E_0 \tag{2}$$

$$\Delta E_{ij} \equiv E_{ij} - \sum_i \Delta E_i - E_0 \tag{3}$$

$$\Delta E_{ijk} \equiv E_{ijk} - \sum_{i<j} \Delta E_{ij} - \sum_i \Delta E_i - E_0 \tag{4}$$

and so on for the higher-body increments. In the butadiene calculations, E_0 is taken as the energy of (either the ground or excited state) with all the orbitals frozen, except for the highest occupied molecular orbital. Thus, when estimating the exact result for 7 frozen orbitals, as in the table, $N = 15 - 1 - 7 = 7$. i.e. there are 7 one-body terms, 21 two-body terms, and so on.

Table 3: Many-body expansion (MBE) energies for the $1^1B_u^+$ transition in eV. The E_0 reference MBE energy correlates only 1 orbital, so with 9 core orbitals the 2-body terms, for example, each involve 3 correlated orbitals. Thus for 9 core orbitals, the 5-body energies would be exact. The 8-core and 9-core results are all available exactly, so we can confirm the convergence of the MBE. Calculations done using `MRCC`.

Core	N-body	CCSD	CCSDT	CCSDTQ	+T	+Q
9	1	7.251	7.165	7.160	-0.086	-0.005
	2	7.206	7.085	7.070	-0.121	-0.015
	3	7.201	7.101	7.085	-0.100	-0.016
	4	7.200	7.098	7.084	-0.101	-0.015
	exact	7.201	7.099	7.083	-0.102	-0.015
8	1	7.133	7.037	7.032	-0.096	-0.006
	2	7.063	6.929	6.908	-0.134	-0.021
	3	7.063	6.975	6.959	-0.088	-0.016
	4	7.071	6.967	6.952	-0.104	-0.015
	exact	7.069	6.966	6.951	-0.103	-0.015
7	1	7.079	6.971	6.966	-0.108	-0.006
	2	7.028	6.896	6.870	-0.132	-0.025
	3	7.034	6.939	6.922	-0.095	-0.018
	4	7.038	6.931	6.917	-0.107	-0.014
	exact	7.038	6.930		-0.108	
6	exact	7.002	6.885		-0.117	
5	exact	6.936	6.819		-0.117	
4	exact	6.919	6.795		-0.124	

Table 3 shows the results of applying the MBE to the $1^1B_u^+$ state to estimate the exact 9-frozen, 8-frozen and 7-frozen orbitals cases. In the case of the first two, we have the exact result, so we

can see that the MBE is converged to less than 0.001 eV with only 3 or 4-body terms included.

Table 4: Many-body expansion (MBE) energies for the $2^1A_g^-$ transition in eV. The E_0 reference MBE energy correlates only 1 orbital, so with 9 core orbitals the 2-body terms, for example, each involve 3 correlated orbitals. The 10-core results are all available exactly, but the remainder are not. Calculations done using `NWChem`.

Core	N-body	CCSD	CCSDT	CCSDTQ	+T	+Q
10	1	7.112	6.684	6.685	-0.428	0.001
	2	7.491	6.982	6.945	-0.509	-0.038
	exact	7.436	6.950	6.918	-0.486	-0.033
9	1	7.134	6.618	6.618	-0.516	0.000
	2	7.673	7.098	7.041	-0.575	-0.057
	exact	7.567	7.023		-0.544	
8	1	7.129	6.540	6.540	-0.589	-0.001
	2	7.706	7.069	6.995	-0.636	-0.074
	exact	7.564	6.981		-0.584	
7	exact	7.610	6.975		-0.635	
6	exact	7.640	6.954		-0.686	
5	exact	7.654	6.900		-0.754	
4	exact	7.648	6.830		-0.818	

In the case of the $2^1A_g^-$ transition, we needed to use `NWChem` due to convergence problems using `MRCC`. The calculations were a little more expensive, therefore, and as shown in Table 2, we needed to use the MBE to estimate the result with both 8 and 9 frozen core orbitals. Table 4 shows how these numbers were obtained. Again, due to expense, we were only able to approximate the MBE up to the 2-body terms. Combined with the fact that the quadruples correction is much more important for the $2^1A_g^-$ state than the $1^1B_u^+$ one, the results are significantly less-well converged. However, it is plausible that the best estimate of -0.074 eV is accurate to within 0.04 eV (chemical accuracy).

Molecular geometries

Our main results are presented using the same experimental geometry as is used widely in previous theoretical studies,[1,2] and derived from the 1966 experimental data of Haugen and Traetteberg.[3] We made this choice to facilitate easier comparison with previous studies, but the choice of geometry could potentially affect the results on a scale of 0.1 eV, so we explored two other theoretically optimized geometries in addition. In particular, assuming C_{2v} symmetry, we optimized the geometry at the MP2/cc-pVQZ and CCSD(T)/aug-cc-pVQZ levels of theory using the `MOLPRO` quantum chemistry package. The coordinates are collated in Table 5 and corresponding excitation energies at the EOM-CCSD level are given in Table 6.

Table 5: Experimental and optimized geometries of *trans*-butadiene used in our studies. Units in Angstrom.

	Experimental			MP2/cc-pVQZ			CCSD(T)/aug-cc-pVQZ		
Atom	x	y	z	x	y	z	x	y	z
C	1.740343	0.616556	0.000000	1.834350	-0.157794	0.000000	1.7414427	0.6171859	0.0000000
C	-1.740343	-0.616556	0.000000	-1.834350	0.157794	0.000000	-1.7414427	-0.6171859	0.0000000
C	0.397343	0.616556	0.000000	0.612753	0.388232	0.000000	0.3998134	0.6099967	0.0000000
C	-0.397343	-0.616556	0.000000	-0.612753	-0.388232	0.000000	-0.3998134	-0.6099967	0.0000000
H	0.126346	-1.577069	0.000000	0.509700	1.466975	0.000000	0.1443398	-1.5501826	0.0000000
H	-0.126346	1.577069	0.000000	-0.509700	-1.466975	0.000000	-0.1443398	1.5501826	0.0000000
H	2.279054	1.568725	0.000000	2.723649	0.452738	0.000000	2.3020010	1.5422423	0.0000000
H	-2.279054	-1.568725	0.000000	-2.723649	-0.452738	0.000000	-2.3020010	-1.5422423	0.0000000
H	2.279054	-0.335614	0.000000	1.961466	-1.231090	0.000000	2.3041193	-0.3093168	0.0000000
H	-2.279054	0.335614	0.000000	-1.961466	1.231090	0.000000	-2.3041193	0.3093168	0.0000000

Table 6: *trans*-butadiene $1^1B_u^+$ and $2^1A_g^-$ EOM-CCSD vertical excitation energies in eV with three different geometries and basis sets.

Basis	Experimental		MP2/cc-pVQZ		CCSD(T)/aug-cc-pVQZ	
	$1^1B_u^+$	$2^1A_g^-$	$1^1B_u^+$	$2^1A_g^-$	$1^1B_u^+$	$2^1A_g^-$
aug-cc-pVDZ	6.389	7.057	6.379	7.09	6.371	7.070
aug-cc-pVTZ	6.365	7.093	6.357	7.12	6.348	7.107
aug-cc-pVQZ	6.362	7.103	6.354	7.133	6.345	7.117

Basis set extrapolations

In the main text, we explain how we use a two-point extrapolation scheme to estimate the complete basis set (CBS) limit. Since this procedure was established as a way to extrapolate correlation energies originally, it is not clear *a priori* that it is reasonable to apply the same scheme to total energies, or excitation energies. However, in Figure 1, we show the fit we used to extrapolate the aug-cc-pVXZ CBS limit for the $1^1B_u^+$ state at the EOM-CCSD level. Although it is clearly not perfect, the line passes within approximately 0.01 eV of all the data points. We also show in Figure 2 that the extrapolation of the EOM-CR-CCSD(T) *increments* follows the proposed fit very well indeed for the case of the $1^1B_u^+$ state using the aug-cc-pVXZ series.

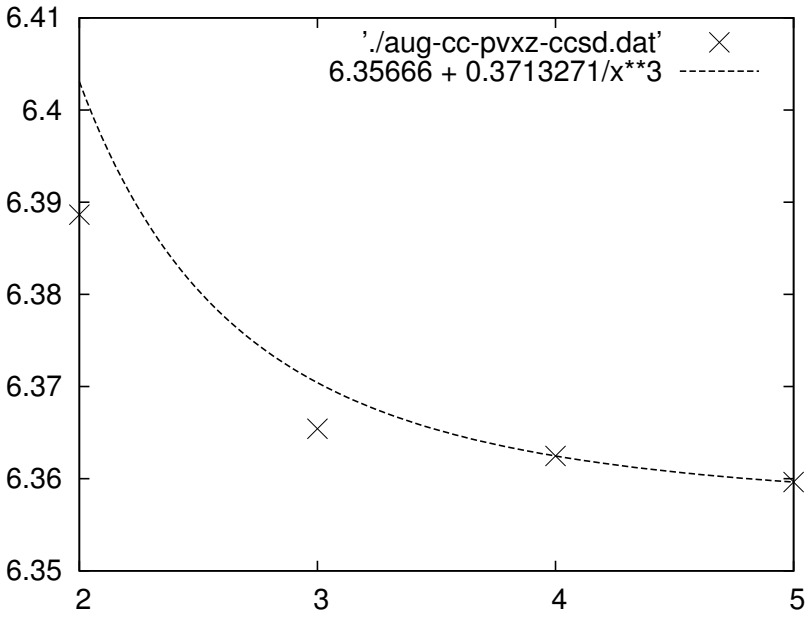

Figure 1: Extrapolation of the EOM-CCSD vertical excitation energies (in eV) for the $1^1B_u^+$ state using the aug-cc-pVXZ series and the two-point $a + b/L^3$ formula, fitting to the highest cardinal numbers.

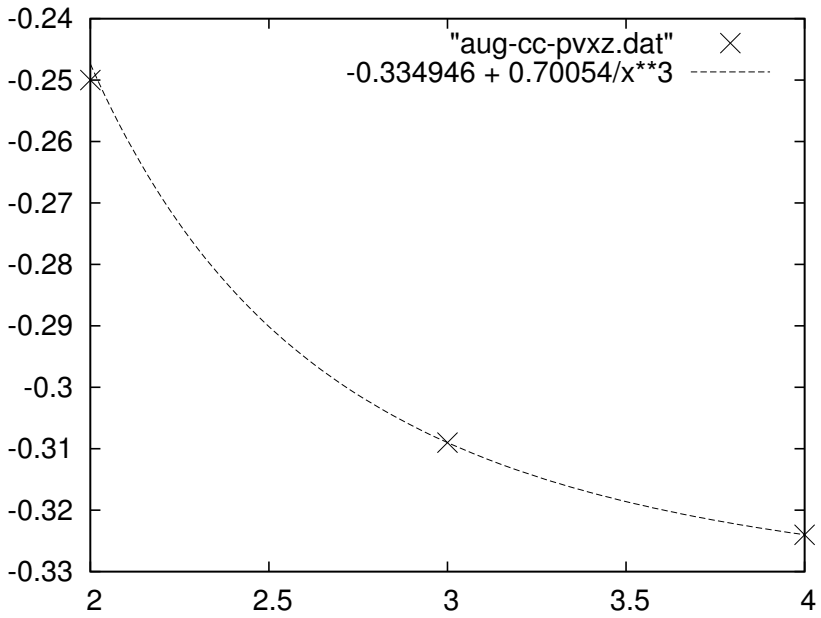

Figure 2: Extrapolation of the EOM-CR-CCSD(T) vertical excitation energy increments (in eV) for the $1^1B_u^+$ state using the aug-cc-pVXZ series and the two-point $a+b/L^3$ formula, fitting to the highest cardinal numbers.

Reinterpretation of the $1^1B_u^+$ experimental data

As discussed in the main text, following Davidson and Jarzecki,[4] interpretation of verticality in the experiment is predicated on several assumptions, in particular high vibrational excitation of the excited state, as well as the validity of the Born-Oppenheimer and Franck-Condon approximations. They suggested that a better estimate of the vertical transition from the experimental measurement could be made by taking the intensity weighted average energy of the transition as the vertical excitation, which is not equivalent to the absorption band maximum when the band is not symmetric.

Table 7: Intensity weighted average energy loss in the electron impact spectra with various incident energies and scattering angles, sampled in the range 5.0–7.2 eV.

Angle /deg	Incident energy/eV	Sampling points	Weighted intensity average/eV
4	13.1	210	5.96
10	13.8	252	5.99
4	43	112	6.01
10	43	163	6.01
20	43	150	6.05

We have carefully reanalyzed the five electron energy loss spectra shown in Figures 1 and 3 of Doering and McDiarmid,[5] with different scattering angle and impact energy. We integrated the date over the full range of the figures; that is, from 5.0 eV to 7.2 eV. Our results are shown in Table 7.

Acknowledgments The authors gratefully acknowledge financial support from the US Department of Energy, Princeton University, and the Sloan, Dreyfus and Packard Foundations.

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